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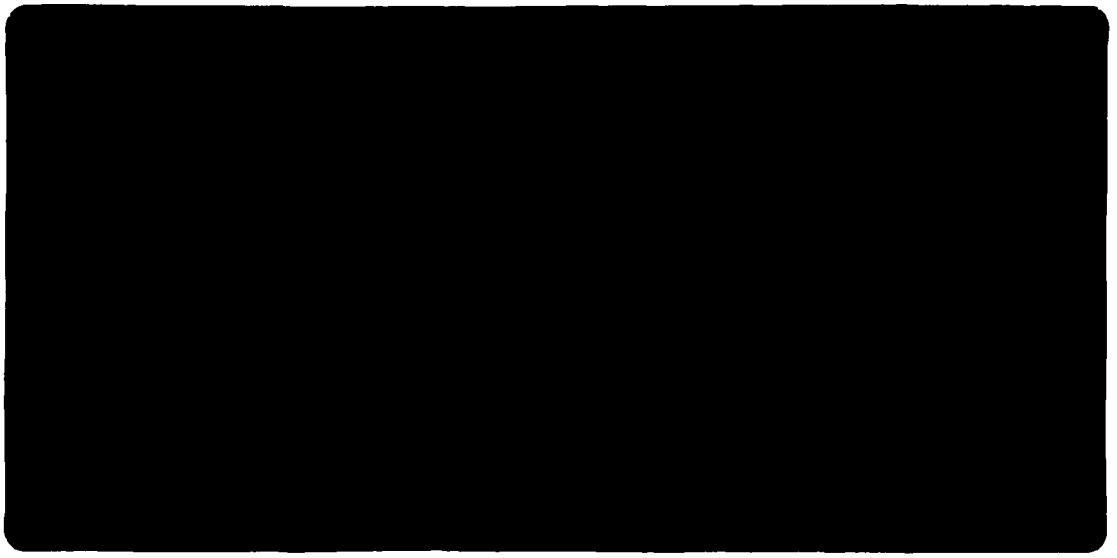

NUMBER 507

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JANUARY 1994

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Submitted to
1994 TAPPI Environmental Conference
April 17–20, 1994
Portland, Oregon

DEVELOPMENT OF A METHOD OF AQUEOUS GEL PERMEATION CHROMATOGRAPHY FOR THE DETERMINATION OF MOLECULAR WEIGHT DISTRIBUTIONS OF BLEACHING EFFLUENTS

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ABSTRACT

A method of aqueous gel permeation chromatography (GPC) was developed and used to determine the molecular weight distributions of bleach plant effluents and ether extracts of the effluents. The method employs two Sephadex G columns in series, elution by 0.1 M LiCl and detection by total organic carbon (TOC) analysis of eluent fractions. Initially, a single column and ultraviolet (UV) detection were used. Subsequent experiments showed that the dual column system gave better separation at low molecular weights. Alkaline eluents, such as NaOH and $NaHCO_3$, caused changes in the apparent molecular weight distributions of acidic stage bleaching effluents, and were therefore considered inappropriate.

The GPC system was calibrated using polyethylene glycols of known molecular weight, and the distributions of several samples determined. The molecular weight distributions of bleaching effluents determined by this method were much lower than those reported for ultrafiltration. The entire (C+D) effluent and over 70% of the E_1 effluent were eluted at relative retention volumes corresponding to molecular weights of less than 1000. The ether extracts of both (C+D) and E_1 stage effluents had distributions that did not exceed 1000.

The method is well suited to bleaching effluents which are comprised mostly of hydrophilic materials. Incomplete recovery was observed only for the most non-polar solutes, found in the ether soluble fraction. This is not serious because the ether extract is a relatively small fraction and is known to contain only low molecular weight components. TOC determination was used for detection because, unlike UV, it is not biased toward strongly UV absorbing solutes. An additional advantage of a universal detection method such as TOC is that it enables determination of the degree to which the sample components are completely recovered from the columns.

INTRODUCTION

Molecular weight distributions of components of the waste streams of pulp manufacture have been determined by ultrafiltration and gel permeation (or size exclusion) chromatography. Ultrafiltration is a method in which solutions of dissolved polymeric materials are filtered under pressure, using membranes with known pore sizes. Small molecules pass through the pores while larger molecules are retained. By using, in succession, a series of such filters, beginning with one that retains only very large molecules and ending with one that only small molecules can pass through, a distribution of molecular size may be found. Ultrafiltration has been used to fractionate kraft black liquor (1, 2). It has also been applied to pulp bleaching effluents for the determination of molecular weight distributions (3-7). Because of possible aggregation and dilution effects, ultrafiltration may give incorrect distributions (8).

Gel permeation chromatography (GPC) is another commonly used method for the determination of molecular weight distributions of solutions of polymeric materials. In GPC, solutions of polymers are separated by molecular size on columns of porous gel material. The gel particles contain pores with a wide distribution of sizes. Large molecules can enter few of the pores, and are eluted first since less of the column volume is available to them. More of the total column volume is available to smaller molecules since they can penetrate more pores in the gel. Small molecules are therefore retained longer in the gel and are eluted later. GPC has been used in the determination of molecular weight distributions for carbohydrates and cellulosics (9-11), lignin model compounds (12, 13), and lignin material from various pulping and bleaching processes (1, 2, 8, 9, 10, 13, 14-24).

Certain factors exist that may lead to elution of polymers not entirely according to molecular size (25). Among these are ion exclusion, ion inclusion, intramolecular electrostatic effects, and adsorption. Most ionic effects can be controlled by increasing the ionic strength of the eluent (25). Another phenomenon observed in GPC of lignins is the formation of association complexes between lignin molecules (14-16). Evidence of association is the occurrence of bimodal molecular weight distribution curves (15, 16). The disappearance of the bimodality is evidence

that association has been eliminated. Commonly used systems that are free of association are Sephadex LH-type gels with 0.1 M LiCl dissolved in DMF as the eluent (16, 19) and Sephadex G-type gels with aqueous NaOH as the eluent (17, 19, 20, 22, 24). Incorporation of the salts in the eluents is believed to cause disruption of association in lignin and lignin-like molecules. Evidence for this is the shift in the distribution toward lower molecular weight and away from bimodality as salt concentration is increased (16, 19).

In the present study, a GPC method for determining molecular weight distributions of bleaching effluent components is considered. This method eliminates the problem of association, has increased resolution, causes minimal time dependent changes in the distributions of acid stage bleaching effluents, and uses a means of detection that is unbiased by the chemical structure of the material. The development of the method is described here and molecular weight distributions for both bleaching effluents and their ether extracts are presented.

EXPERIMENTAL APPROACH

The majority of the experiments were done using mill produced (C+D) and E_1 stage effluents. Polyethylene glycols, sulfonated polystyrenes, and various low molecular weight compounds were used as standards. The results reported here will focus on the distributions of effluent components under different GPC conditions. Calibration of the GPC system is considered in detail only with regard to the final system. Enough eluent solute was added to all standards and effluent solutions to adjust the concentration of these solutions to that of the original eluent.

Various GPC conditions were investigated: single columns, columns in series, different eluent systems, and different eluent flow rates. The retention time of a given solute (or equivalently, the volume of eluent required to elute it) is inversely related to its molecular size, but also depends on the conditions of the separation. In particular, eluent pH changes will result in altered retention time due to gel shrinkage and swelling.

To account for differences in retention under different operating conditions, all gel permeation chromatograms were normalized to relative retention volume scales. The scales were based on the retention of a high molecular weight compound that is completely excluded from pores in the gel, and a low molecular weight compound that is, in theory, completely included in all pores. Relative retention volume is calculated as follows:

$$\text{Relative Retention Volume} = R_s - R_h \,/\, R_l - R_h$$

where

R_s = retention volume of sample.

R_l = retention volume of low molecular weight standard.

R_h = retention volume of high molecular weight standard.

The high molecular weight standard corresponds to a relative retention volume of 0.0 on this scale, and the low molecular weight standard to a value of 1.0. Two different low molecular weight materials were used to estimate R_l: dimethoxybenzoic acid was used when detection was by UV absorbance, and methanol was used when detection was by total organic carbon (TOC) determination. The dimethoxybenzoic acid was not eluted solely on a molecular weight basis, as will be shown later, and was therefore a poor choice. The same retention scale was used within each set of experiments, so comparisons within each set are valid. However, the two relative retention volume scales are not directly comparable. Only in the final experiments, in which detection was by TOC analysis, do molecular weight values correspond directly to the relative retention volume scale.

RESULTS AND DISCUSSION

The objective of the experiments was to develop a method of gel permeation chromatography that was applicable to the determination of molecular weight distributions for pulp bleaching effluents. An ideal method should give accurate molecular weight distributions which are not altered by adsorption to the gel or by associative effects. It should also have good resolution and be reproducible.

The starting point for method development was the work of Sagfors and Starck (22), who used Sephadex G-50 gel and eluted bleaching effluent components from the column with 0.5 M NaOH. Systems of this type have been commonly used in determinations of molecular weight distributions of alkaline pulping waste (17, 19, 20), and molecular association was shown to be negligible (17).

Single Column GPC

In the early stage of the work, a single column containing Sephadex G-50 gel was used, and solutes were eluted with 0.5 M NaOH and detected by UV absorbance at 280 nm. The resulting GPC chromatograms for (C+D) and E_1 stage effluents are shown in Figures 1 and 2. These distributions are very similar to those obtained by Sagfors and Starck.

Concerns about the possibility of causing chemical changes in acid stage bleaching effluents by elution with alkaline systems, led to a consideration of other eluents. Elution with water gave single large peaks at the retention volume of the high molecular weight standard, indicating associative effects. A 0.1 M aqueous LiCl eluent gave similar distributions to those obtained with 0.5 M NaOH (Figures 1 and 2), indicating that LiCl broke the previously observed associations. To increase the UV absorbance of the effluents, $NaHCO_3$ was added to the LiCl eluent, and the distributions were again obtained (Figures 1 and 2). They are similar to the ones obtained using the other eluents. Although some differences may be seen, few distinguishing characteristics exist. This is not surprising since the G-50 gel only has the ability to separate compounds with molecular weights above 1,500.

Dual Column GPC

To increase resolution, particularly at low molecular weights, 2 columns were used in series. The first was packed with Sephadex G-50, as before, and the second was packed with Sephadex G-15. The G-50 gel has the capability to separate solutes having molecular weights of 30,000 to 1,500, and the G-15 gel has separation capability below 1,500. By connecting the columns in series, those compounds not resolved by the first column are separated by the second, and those separated by the first column pass unchanged through the second.

Distributions for the effluents were obtained using the dual column system, with the same 3 eluents studied with the single column. The distributions for the (C+D) effluent are shown in Figure 3 and those for the E_1 effluent are shown in Figure 4. Based on the (C+D) effluent distributions, it is clear that the 2 column system gives increased separation at the low molecular weight end of the distributions. The (C+D) effluent distributions from the 3 sets of conditions are easily distinguishable from one another. The E_1 stage distributions also gain distinguishing features at low molecular weights.

Different eluents gave widely varying distributions for the (C+D) stage effluents, as shown by Figure 3. It was unclear which, if any, of the distributions were correct. During the course of these experiments it was discovered that the distributions obtained with the 0.1 M LiCl/0.1 M $NaHCO_3$ eluent changed as the (C+D) effluent was contacted with the eluent solutes for different lengths of time. A sample of the (C+D) stage effluent was adjusted to 0.1 molarity in both $NaHCO_3$ and LiCl and the sample distribution was determined immediately after sample preparation, several days after sample preparation, and again several weeks later. The results are shown in Figure 5. The distribution shifted toward higher apparent molecular weights as exposure time to the eluent solutes increased. In fact, after an extended exposure time, the distribution became similar in appearance to that obtained using the 0.5 M NaOH (Figure 6). These effects may be due to associative behavior. Although alkaline solutions can eliminate associative behavior, incubation in alkaline solutions can also allow association to occur (15). Similar associative behavior of the (C+D) stage bleaching effluent may occur in solutions of both 0.5 M NaOH and 0.1 M LiCl/0.1 M $NaHCO_3$. However, in the bicarbonate case, the association process may be slow enough to be observed by a sequence of distributions determined after different exposure times. The use of alkaline eluents for the determination of molecular weight distributions of (C+D) or other acidic stage bleaching effluents is clearly unsatisfactory.

GPC With TOC Detection

All previous distributions had been obtained by using a flow-through UV absorbance detector. UV detection is dependent on chemical structure of the solute, and biases distributions toward highly absorbing materials. An alternative is TOC analysis. TOC measures the amount of organic carbon, unbiased by chemical structure.

In this group of experiments, the relative retention volume scale was based on a high molecular weight polyethylene glycol and methanol. The relative retention volume for a series of polyethylene glycol (PEG) standards and methanol are given in Table I. Samples were collected as they emerged from the columns, and each sample was individually analyzed for TOC.

The first experiment was a determination of (C+D) effluent stability to the 0.1 M LiCl eluent. The (C+D) effluent was prepared, run immediately, then run again after 9 days. Although the two distributions are not identical (Figure 7), they are very similar, and are much more reproducible than when alkaline eluents were used.

The (C+D) and E_1 effluents were analyzed by this system and the distributions are shown in Figure 8. Cumulative molecular weight distributions for the effluents are shown in Figure 9. Each point in the cumulative distribution shows the percentage of effluent TOC corresponding to a molecular weight less than the given molecular weight. As expected, the (C+D) effluent contains a greater percentage of low molecular weight components. The entire (C+D) effluent consists of material with an apparent molecular weight of less than 1000. About 70% of the E_1 effluent is eluted at a relative retention volume corresponding to a molecular weight less than 1000. In fact the peak that occurs in the E_1 stage distribution, between relative retention values of 0.7 and 0.9, corresponds to material with molecular weights of less than 300. This is contrary to earlier results obtained by ultrafiltration in which far more high molecular weight material was found (3-7). The latter result may be explained in terms of concentration dependent clogging of membranes which inhibits the passage of low molecular weight material (8).

It is interesting to compare the E_1 effluent distribution obtained by UV absorption with that obtained by TOC analysis. Such a comparison (Figure 4 compared to Figure 8) indicates that the high molecular weight E_1 stage material absorbs UV strongly while the lower molecular weight material absorbs very little. Similar arguments may be made for the (C+D) stage effluent distributions.

Ether extracts of bleaching effluents have been isolated and characterized because the majority of compounds of environmental interest are ether soluble (26). Ether extracts of both effluents were prepared, dissolved in water, the ether removed, and the molecular weight distributions determined. These distributions are shown in Figure 10. The ether extractable effluent material is apparently of low molecular weight (almost entirely less than 300), as expected on the basis of earlier work, which showed the number average molecular weight of ether extracts to be less than 300 (27).

Characterization of the Dual Column System

A variety of standards were run and a calibration curve made for the dual column system. Polyethylene glycol (PEG) standards covering a wide range of molecular weights (106-19,700) were used as standards when TOC was the means of detection. Since material in bleaching effluents has been shown to be largely aliphatic and highly oxidized (3, 4), PEG should be a reasonable model of residual lignin after bleaching. Sulfonated polystyrene standards (SPS), which were used during the UV detection experiments, and a variety of low molecular weight acids were also run to calibrate this system. The calibration curve is shown in Figure 11. Surprisingly the PEG and SPS standards fall on the same curve even though they differ greatly in structure. Several acids known to exist in effluents (acetic, chloroacetic, oxalic, malonic, and succinic acids) and others of a similar type (muconic and adipic acids) fall on or very near the curve. Others (azelaic acid and dimethoxybenzoic acid) are far from the curve.

It is clear from these results, that dimethoxybenzoic acid was a poor choice for a low molecular weight standard in the early experiments, since it does not elute solely on the basis of molecular size. Its elution behavior is determined by a combination of molecular size and attraction to the gel. The compounds which fall far from the calibration curve were quite water insoluble, and were therefore more non-polar and more likely to adsorb to the gel column than the more water soluble species. Highly polar, highly water soluble molecules move through the column and are separated on the basis of molecular size, while non-polar, water insoluble compounds are adsorbed to varying extents on the gel and are eluted at longer than expected times, or in extreme cases not eluted at all.

Further support for this theory is provided by the recovery of TOC after fractionation by GPC. An advantage of TOC detection is that it allows a measurement of TOC recovery from the columns after fractionation. If no adsorption to the column occurs, the sum of TOC in all fractions should equal that of the initial effluent sample before fractionation. The ether extractable effluent material, which is the most non-polar effluent fraction and the most water insoluble fraction (distributions seen in Figure 10), had TOC recoveries of only 42 and 66% for the (C+D) and E_1 effluents, while recoveries for the effluent components

not extracted by ether were 100% or greater. Any recovery greater than 100% may have been the result of adsorbed material removal by additional elution. Because of solute losses and the resulting contamination of the columns, this system is not well suited to the ether extracts. The GPC method using Sephadex gels and 0.1 M aqueous LiCl eluent is most valid for polar materials, for example non-ether extractable effluent fractions, or effluents from ClO_2, oxygen, or ozone bleaching.

Due to adsorption effects, the whole effluent distributions (Figure 9) may be altered somewhat. However, since the amount of the ether extractable TOC is generally 10% or less of the total TOC (26), the effect should be small. Since any adsorbed material is likely to be ether extractable and therefore of low molecular weight, the low molecular weight end of the distributions are probably affected most.

EXPERIMENTAL METHODS

Sample Preparation

Bleaching effluents were mill produced, and ether extracts were collected as discussed elsewhere (26). Eluent solutes were added to all samples to adjust them to the same concentration as the eluents. The sample pH was also adjusted to the pH of the eluent system. When TOC detection was implemented, samples were acidified to pH 2, the samples sparged with nitrogen to eliminate carbonate, and the sample pH adjusted upward to that of the LiCl eluent (pH 5.0-5.5).

Gel Preparation and Column Packing

Sephadex G-type gels, made of crosslinked dextran, were used for GPC work. The gels were purchased in a powdered state, were swelled first in water and then in the eluent system, before column packing. Pharmacia HR 16/50 columns were used for GPC work, and a HR 16 column packing reservoir used during the packing process. Each column was packed individually. The swelled gel was added to the column and the packing reservoir and the gel was packed into the column using flow rates and pressures in excess of those used during chromatography experiments. At least 2 column volumes of eluent (200 ml) was passed through the columns under these conditions to stabilize the gel bed. Once the bed was stable, the column top adapter was attached and the columns were used.

Gel Permeation Chromatography

Chromatography and column packing were done using a Varian Model 5000 HPLC. When UV detection was used, the flow from the columns passed directly into the UV detector associated with the instrument. When TOC detection was used, 100 separate 3 ml samples were collected in a fraction collector, and the TOC determined for each. Flow rates of 0.5 ml/min were used in the UV detection studies, while 1 ml/min flow rates were used for TOC detection experiments.

TOC Analysis

Measurement of TOC was done using a Beckman model 915-B Tocamaster analyzer. The instrument was calibrated using standard solutions of potassium hydrogen phthalate.

SUMMARY AND CONCLUSIONS

A method of aqueous gel permeation chromatography has been developed and applied to mill produced bleaching effluents and ether extracts of the effluents. The method uses 2 Sephadex G-type gel columns in series - one to separate high molecular weight material and the other to separate materials of low molecular weight. The eluent system is 0.1 M LiCl, and detection is done by total organic carbon analysis. The dual column system gives improved low molecular weight separation compared to a single column system, and 0.1 M LiCl does not cause changes in the distributions of acidic stage effluents as alkaline eluent systems do. TOC analysis provides detection that is unbiased by the chemical structures of eluted material, unlike UV detection.

The method was found to be most appropriately used for hydrophilic materials, since such materials have minimal interaction with the column. In the present study the method was used to estimate the molecular weight distribution for bleaching effluents and ether extracts of effluents, although the system is not ideally suited to ether extracts. The effluent distributions were of a much lower molecular weight than those reported for ultrafiltration. All (C+D) effluent components had molecular weights of less than 1000, as did about 70% of the E_1 stage effluent. The ether extracts from both stages were entirely below 1000.

ACKNOWLEDGMENTS

The authors thank Dr. Earl Malcolm and Dr. Lucy Sonnenberg for technical advice and guidance, and the Institute of Paper Science and Technology and its member companies for supporting this research. This work will be used by T. S. as partial fulfillment of the requirements for the Ph.D. degree at the Institute of Paper Science and Technology.

LITERATURE CITED

1. Hill, M. K., *Department of Energy Report,* "Ultrafiltration of Kraft Black Liquor," Final Report-Phase I, DOE/CE/40606-T3, October 1985.

2. Hill, M. K., *Department of Energy Report,* "Ultrafiltration of Kraft Black Liquor," Final Report-Phase II, DOE/CE/40606-T4, September 1987.

3. Lindstrom, K., Osterberg, F., *Holzforschung,* "Characterization of the High Molecular Mass Chlorinated Matter in Spent Bleach Liquors (SBL) Part 1. Alkaline SBL," 38(4):201 (1984).

4. Osterberg, F., Lindstrom, K., *Holzforschung,* "Characterization of the High Molecular Mass Chlorinated Matter in Spent Bleach Liquors (SBL) Part II. Acidic SBL," 39(3):149 (1985).

5. Hardell, H. L., de Sousa, F., *Svensk Papperstidning,* "Characterization of Spent Bleaching Liquors, Part 1. Spent Liquors From the Chlorine and Alkali Extraction Stages in the Prebleaching of Pine Kraft Pulp," 1977(4): 110.

6. Pfister, K., Sjostrom, E., *Paperi ja Puu,* "Characterization of Spent Bleaching Liquors, Part 2. Composition of Material Dissolved During Chlorination (CEH Sequence)," 1979(4a): 220.

7. Pfister, K., Sjostrom, E., *Paperi ja Puu,* "Characterization of Spent Bleaching Liquors, Part 6. Composition of Material Dissolved During Chlorination and Alkaline Extraction (OCE Sequence)," 1979(10): 619.

8. Jokela, J. K., Salkinoja-Salonen, M., *Environmental Science and Technology,* "Molecular Weight Distributions of Organic Halogens in Bleached Kraft Pulp Mill Effluents," 26(6): 1190 (1992).

9. Collins, J. W., Webb, A. A., Boggs, L. A., *Tappi,* "Characterization of Lignin and Carbohydrate Residues Found in Bleach Effluents," 54(1): 105 (1971).

10. Collins, J. W., Webb, A. A., *Tappi,* "Detection and Gel Chromatography of Carbohydrates in Pulp Mill Effluents," 55(9): 1335 (1972).

11. Barth, H. G., Regnier, F. E., *Journal of Chromatography,* "High Performance Gel Permeation Chromatography of Water Soluble Cellulosics," 1980(192): 275.

12. Connors, W. J., Lorenz, L. F., Kirk, T., *Holzforschung,* "Chromatographic Separation of Lignin Models by Molecular Weight Using Sephadex LH-20," 32(3): 106 (1978).

13. Connors, W. J., *Holzforschung,* "Gel Chromatography of Lignins, Lignin Model Compounds, and Polystyrenes Using Sephadex LH-60," 32(4): 145 (1978).

14. Sarkanen, S., Teller, D. C., Abramowski, E., Mc Carthy J. L., *Macromolecules,* "Lignin 19. Kraft Lignin Component Conformation and Associated Complex Configuration in Aqueous Alkaline Solution," 1982(15): 1098.

15. Sarkanen, S., Teller, D. C., Hall, J., Mc Carthy, J. L., *Macromolecules,* "Lignin 18. Associative Effects Among Organosolv Lignin Components," 1981(14): 426.

16. Connors, W. J., Sarkanen, S., Mc Carthy, J. L., *Holzforschung,* "Gel Chromatography and Association Complexes of Lignin," 34(3): 80 (1980).

17. Ohi, H., Ishizu, A., *Mokuzai Gakkaishi,* "Behavior of Lignin During Alkaline Sulfite-Quinone Cooking II," 35(8): 748 (1989).

18. Obiaga, T. I., Wayman, M., *Journal of Applied Polymer Science,* "Improved Calibration Procedures for Gel Permeation Chromatography of Lignins," 1974(18): 1943.

19. Forss, K., Janson, J., Sagfors, P. E., *Paperi ja Puu,* "Influence of Anthraquinone and Sulfide on the Alkaline Degradation of the Lignin Macromolecule," 1984(2): 77.

20. Forss, K. G., Stenlund, B. G., Sagfors, P. E., *Applied Polymer Symposium,* "Determination of the Molecular Weight Distribution of Lignosulfonates and Kraft Lignins," 1976(28): 1185.

21. Pellinen, J., Salkinoja-Salonen, M., *Journal of Chromatography,* "Aqueous Size Exclusion Chromatography of Industrial Lignins," 1985(322): 129.

22. Sagfors, P. E., Starck, B., *Water Science and Technology,* "High Molar Mass Lignin in Bleached Kraft Pulp Mill Effluents," 20(2): 49 (1988).

23. Hakulinen, R., Salkinoja-Salonen, M., *1982 International Pulp Bleaching Conference Proceedings,* "Treatment of Kraft Bleaching Effluents: Comparison of Results Obtained by Enso-Fenox and Alternative Methods," pp. 97-106.

24. Ohi, H., McDonough, T. J., *Mokuzai Gakkaishi,* "Mechanisms of Nitrogen Dioxide Pretreatment for Oxygen Bleaching of Kraft Pulp II," 38(7): 707 (1992).

25. Barth, H. G., *Journal of Chromatographic Science,* "A Practical Approach to Steric Exclusion Chromatography of Water-Soluble Polymers," 1980(18): 409.

26. Schwantes, T. A., McDonough, T. J., *1993 Tappi Pulping Conference Proceedings,* "Characterization of Effluent Fractions From ClO_2 and Cl_2 Bleaching of Unbleached and O_2 Bleached Softwood Kraft Pulps."

27. Sameshima, K., Simson, B., Dence, C. W., *Svensk Papperstidning,* "The Fractionation and Characterization of Toxic Materials in Kraft Spent Bleaching Liquors," 83(6): 162 (1979).

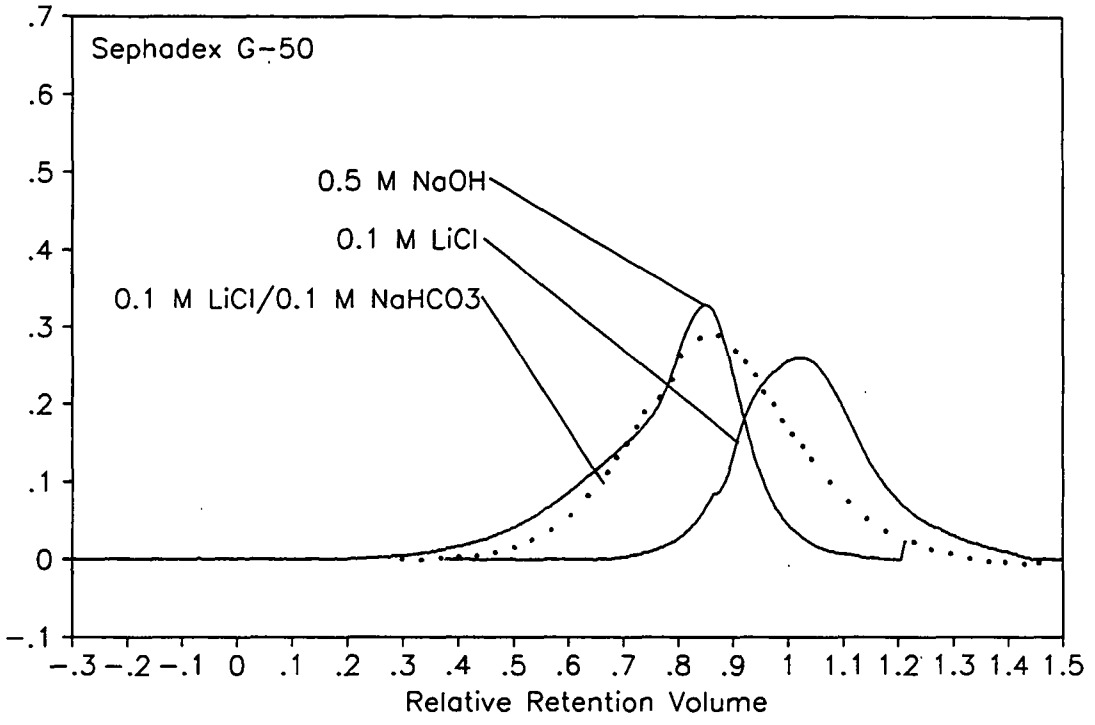

Figure 1. Single Column GPC of (C+D) Stage Effluent.

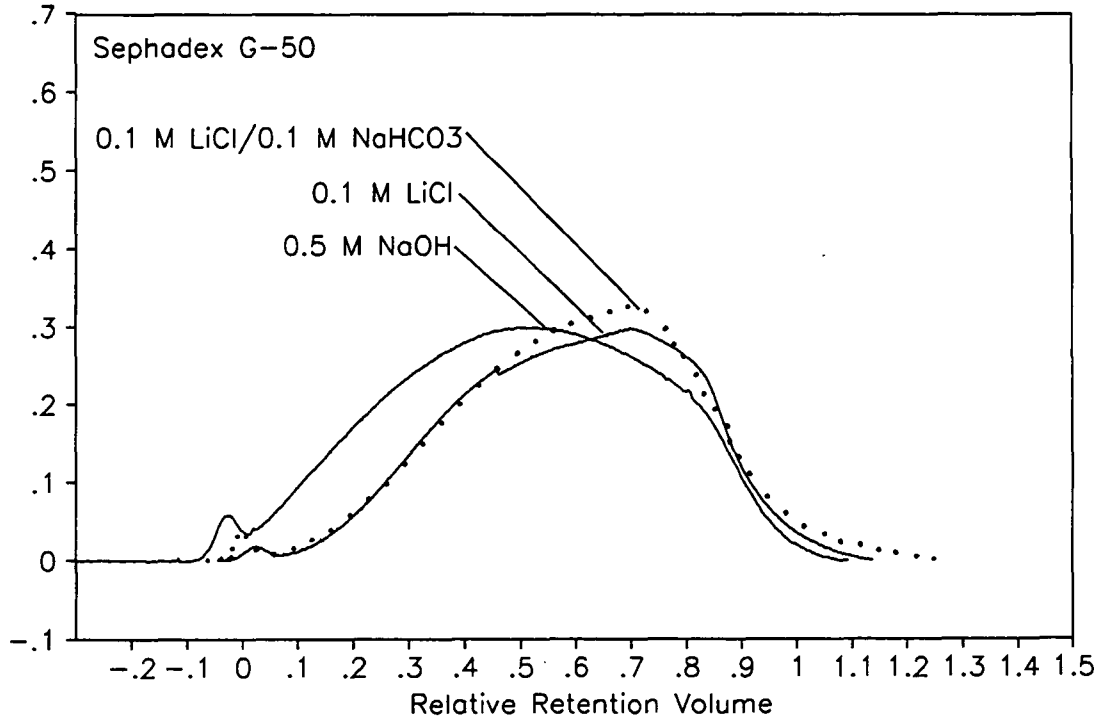

Figure 2. Single Column GPC of E1 Stage Effluent.

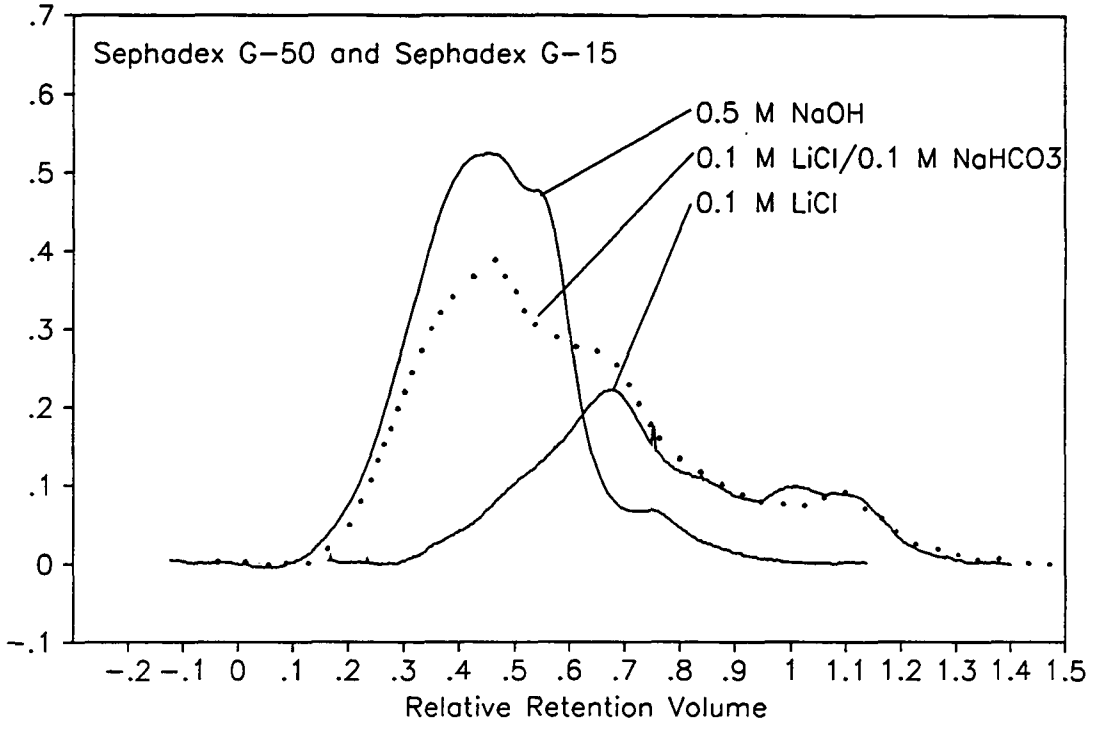

Figure 3. Dual Column GPC of (C+D) Stage Effluent.

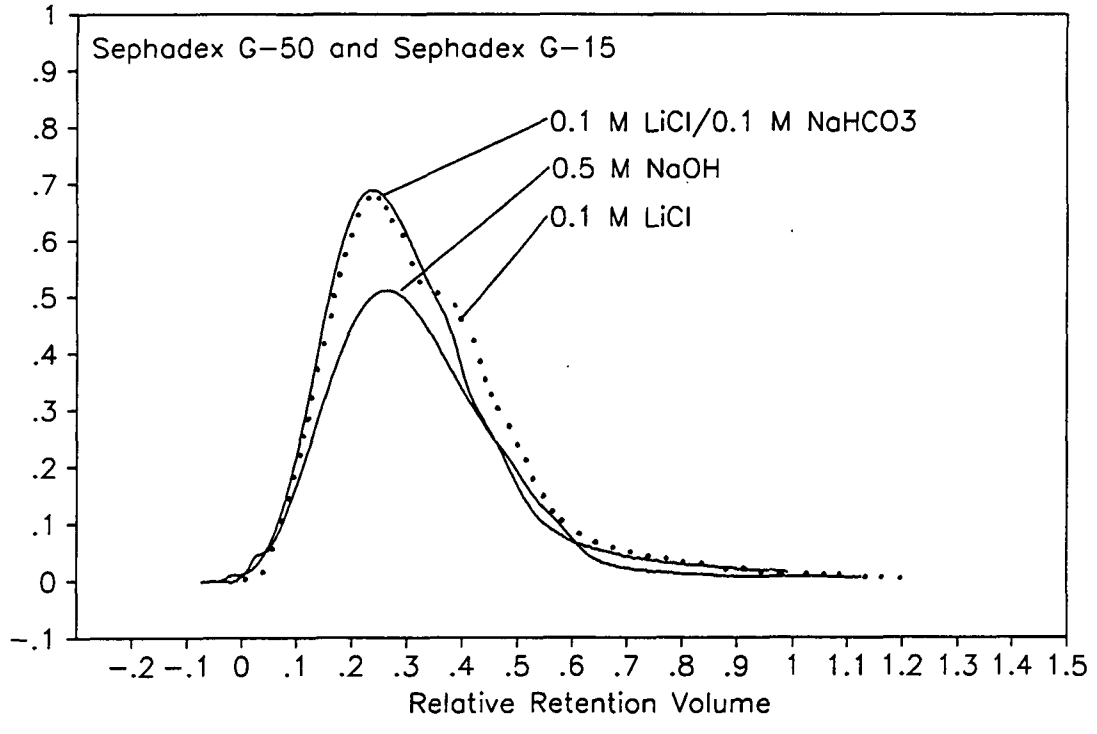

Figure 4. Dual Column GPC of E1 Stage Effluent.

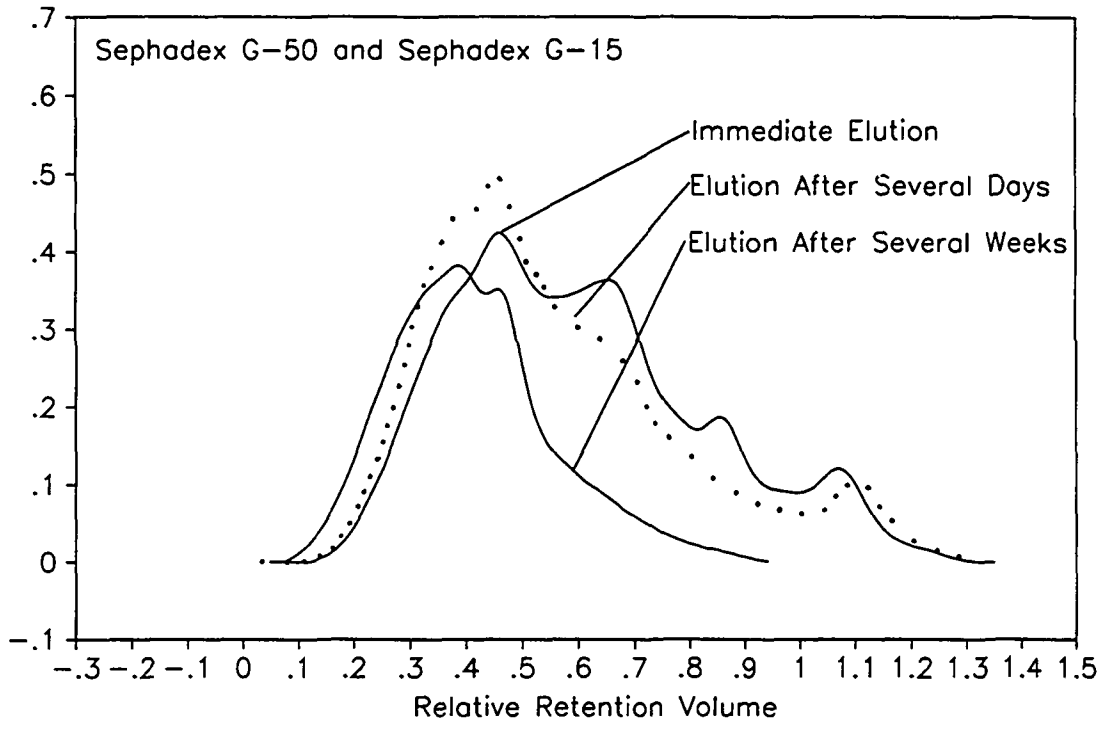

Figure 5. GPC of (C+D) Effluent After Different Storage Times in 0.1 M LiCl/0.1 M NaHCO3.

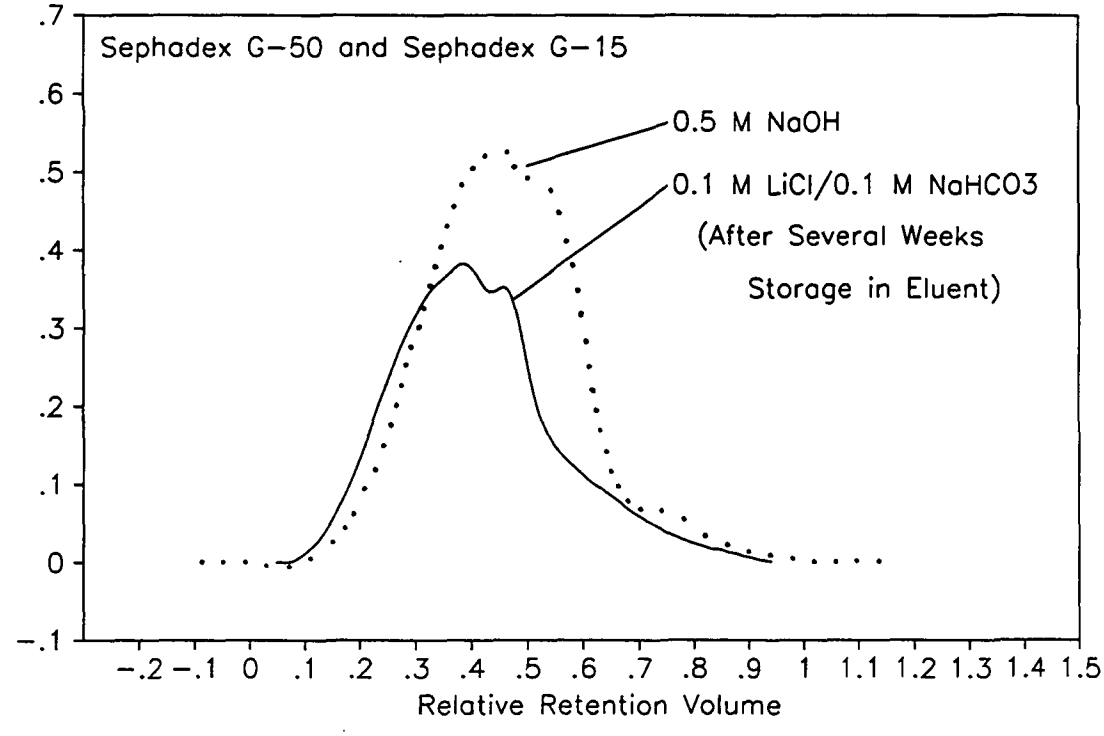

Figure 6. GPC Comparison of (C+D) Effluent–0.5 M NaOH Compared to Long Storage Time in 0.1 M LiCl/0.1 M NaHCO3.

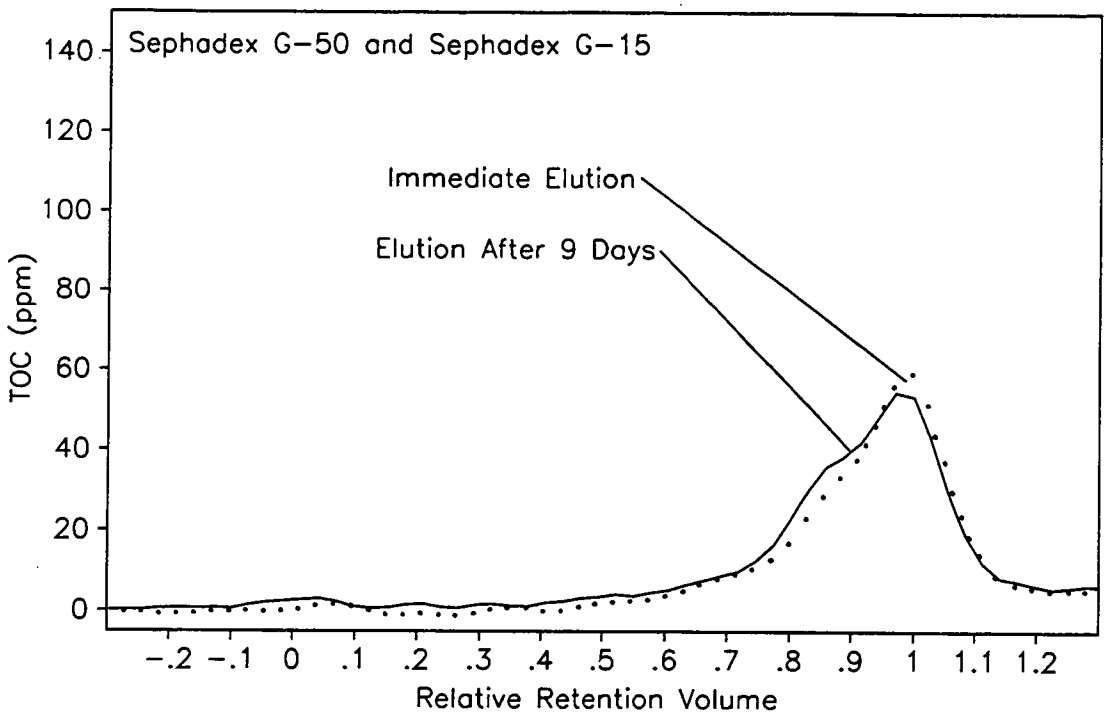

Figure 7. GPC of (C+D) Effluent After Storage in 0.1 M LiCl.

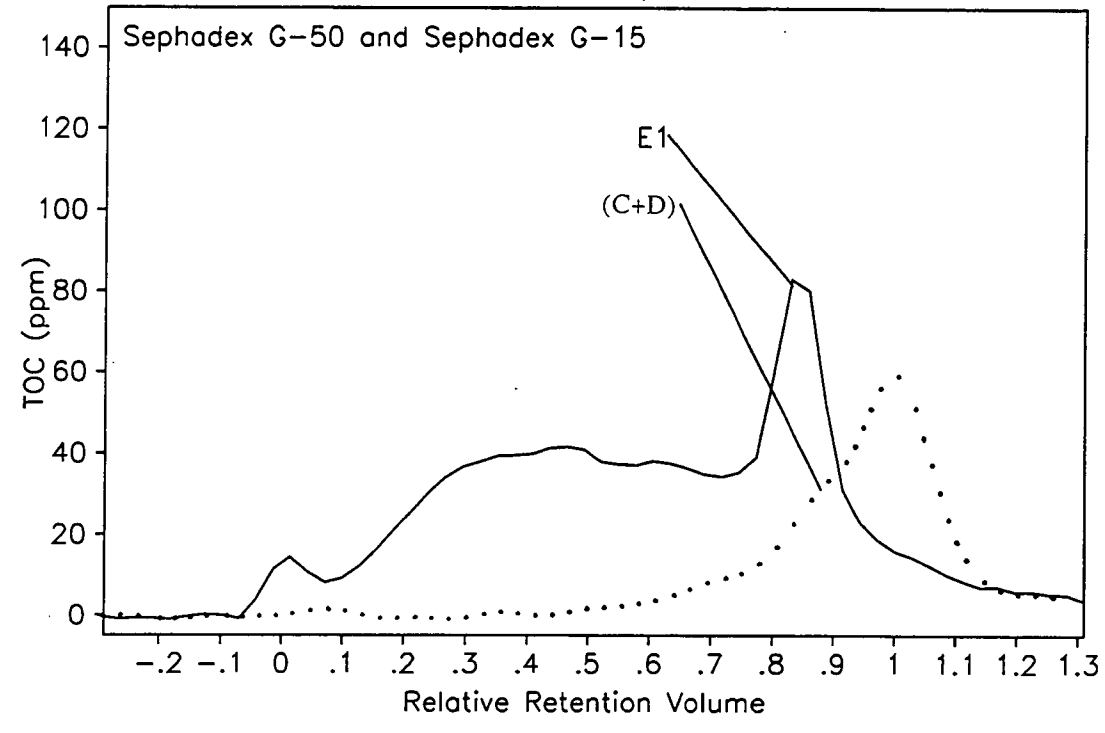

Figure 8. GPC of Effluents with TOC Detection.

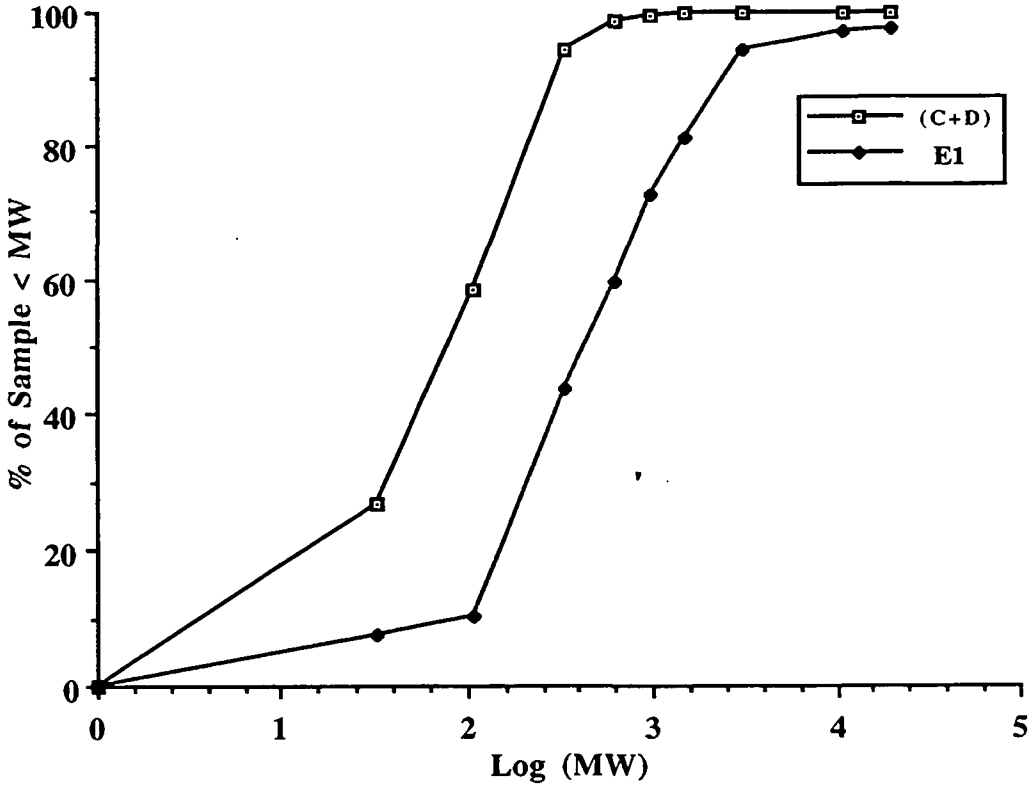

Figure 9. Cumulative Molecular Weight Distributions for Effluents.

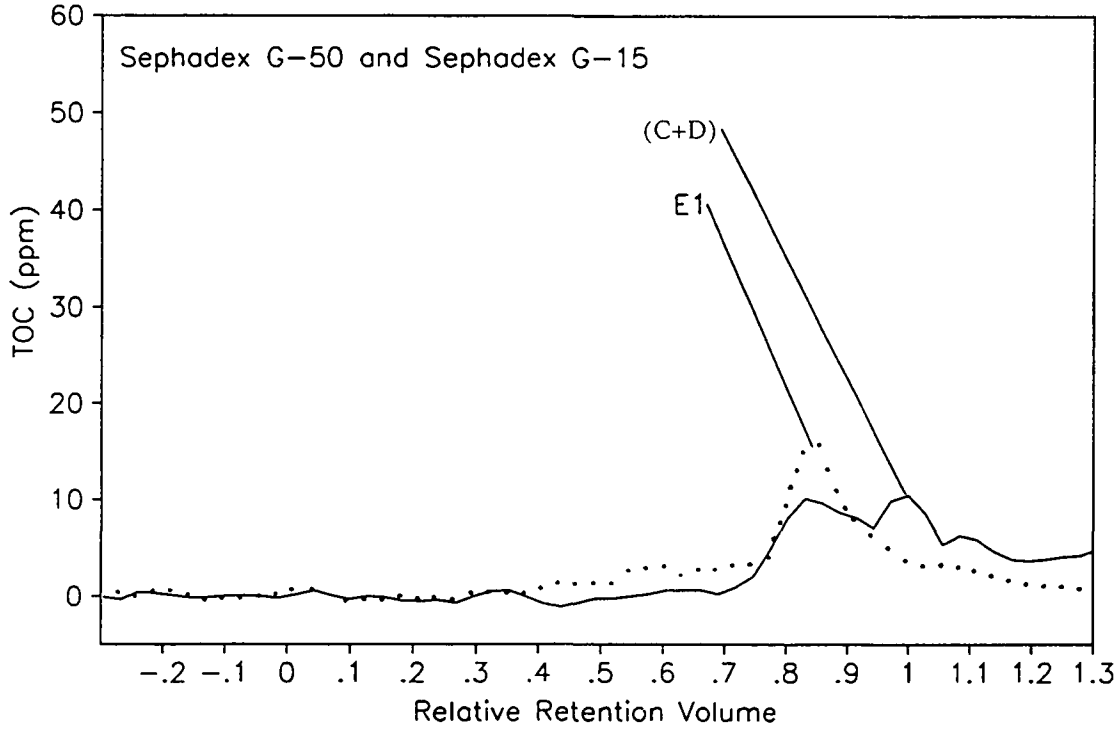

Figure 10. GPC of Ether Extracts.

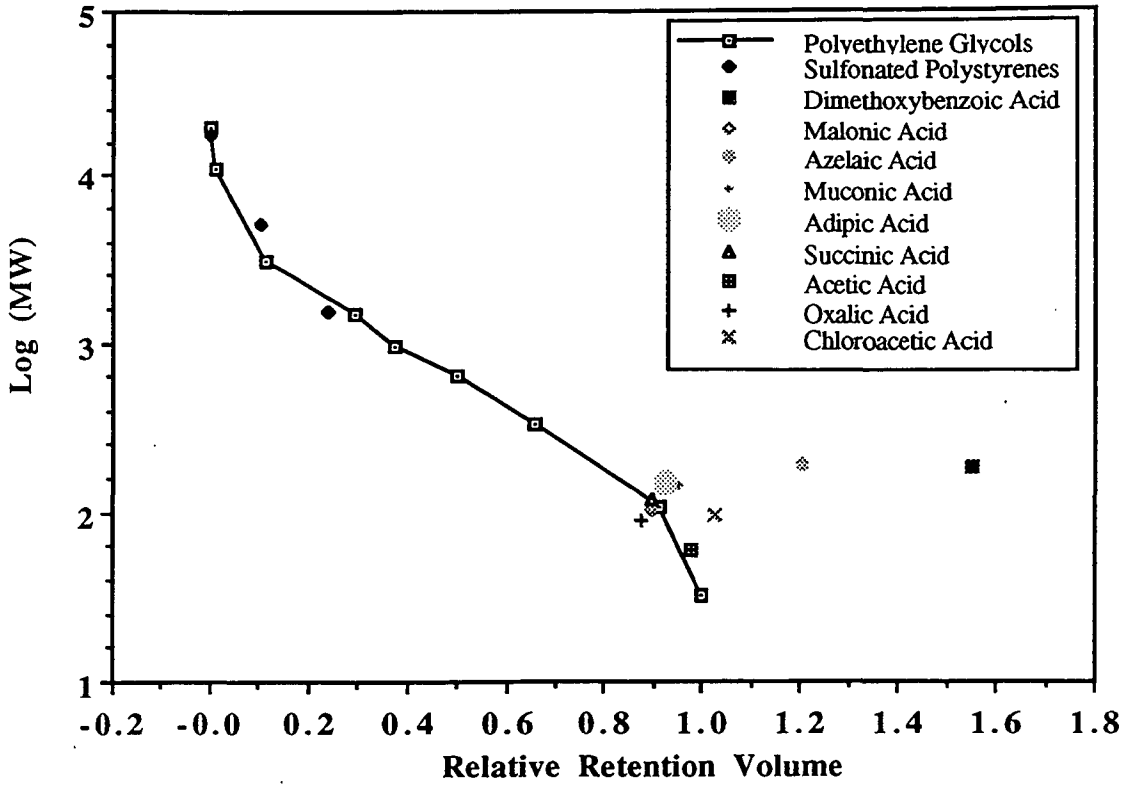

Figure 11. Calibration Curve for Dual Column System.

Table I. Elution of PEG Standards and Methanol.

Molecular Weight	Relative Retention Volume
19,700	0.000
10,900	0.013
3,070	0.115
1,490	0.295
960	0.372
629	0.500
331	0.654
106	0.910
32	1.000